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<sup>(12)</sup>UK Patent Application <sup>(19)</sup>GB <sup>(11)</sup> 2 1 1 4 5 9 4 A

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(21) Application No 8303000

(22) Date of filing

3 Feb 1983

(30) Priority data

(31) 347854

(32) 11 Feb 1982

(33) United States of America  
(US)

(43) Application published

24 Aug 1983

(51) INT CL<sup>3</sup> C10G 47/16  
47/20

(52) Domestic classification  
C5E DS

(56) Documents cited

GB 1506429

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US 3367884

(58) Field of search

C5E

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(54) Middistillate production

(57) A process for selectively producing middistillate hydrocarbons comprises:

(a) contacting under hydrocracking conditions a hydrocarbonaceous feed boiling above 600°F (316°C) with a catalyst comprising a hydrogenation component and an expanded pore zeolite which consists of a faujasitic zeolite which has been steamed and then dealuminated; and

(b) recovering a hydrocarbonaceous effluent of which more than 40 percent by volume boils above 300°F (149°C) and below 700°F (371°C).

The faujasitic zeolite can be a Y or X-type zeolite which is preferably an ultrastable Y zeolite having a sodium oxide content of less than 0.5 wt.%. The steamed zeolite can

be dealuminated by treatment with acid or with an organic chelating agent such as EDTA. The process can advantageously be operated as the first stage of a two-stage hydrocracking scheme.

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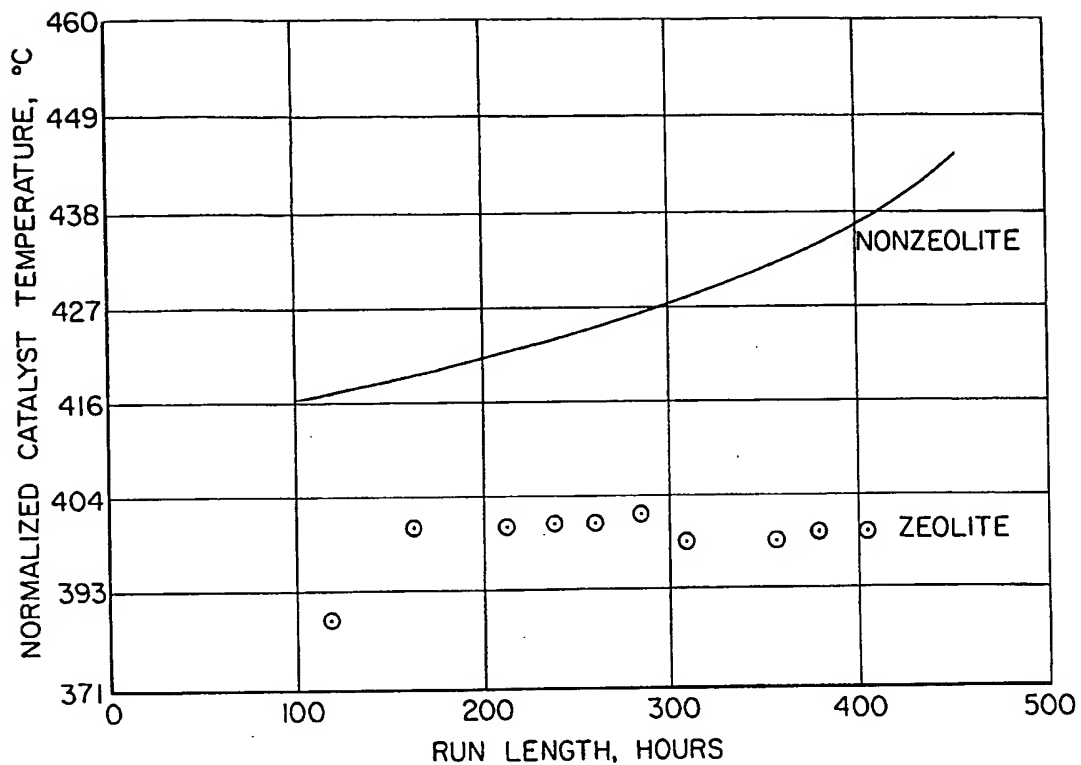


FIG.\_1.

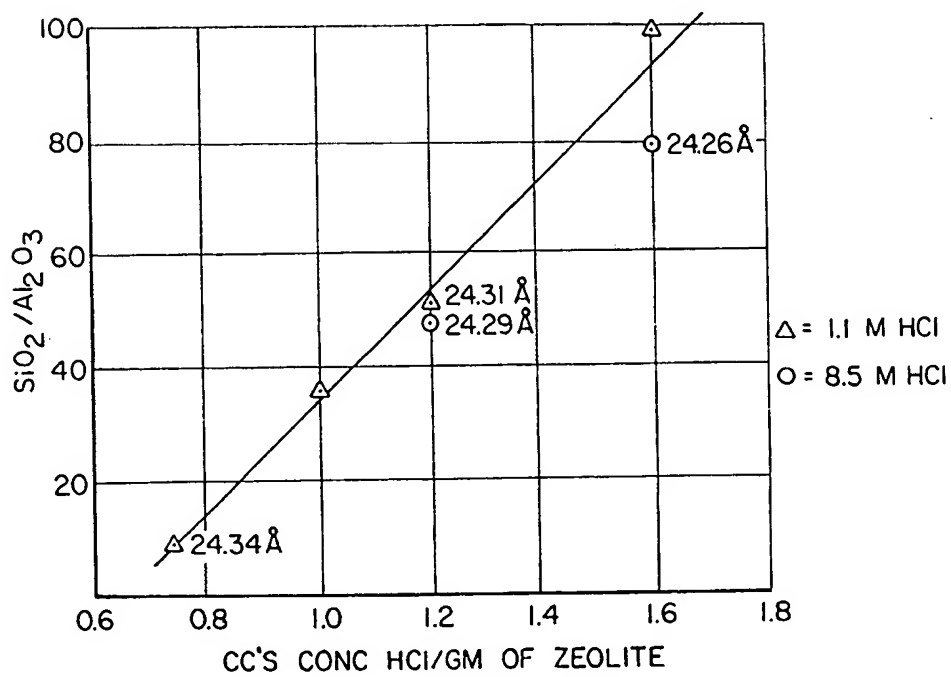


FIG.\_2.

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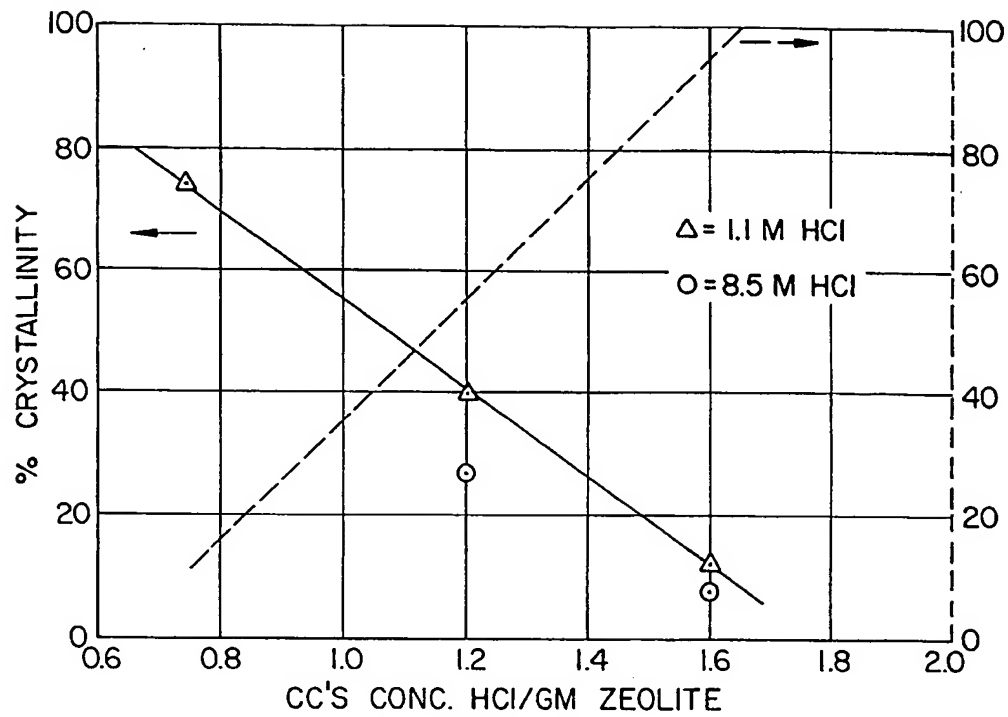


FIG. 3.

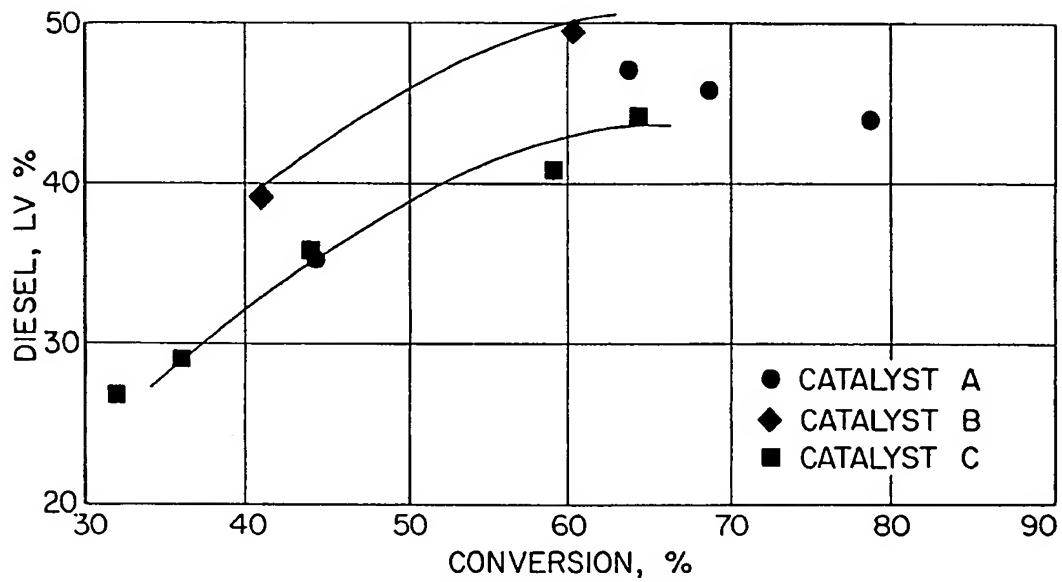


FIG. 4.

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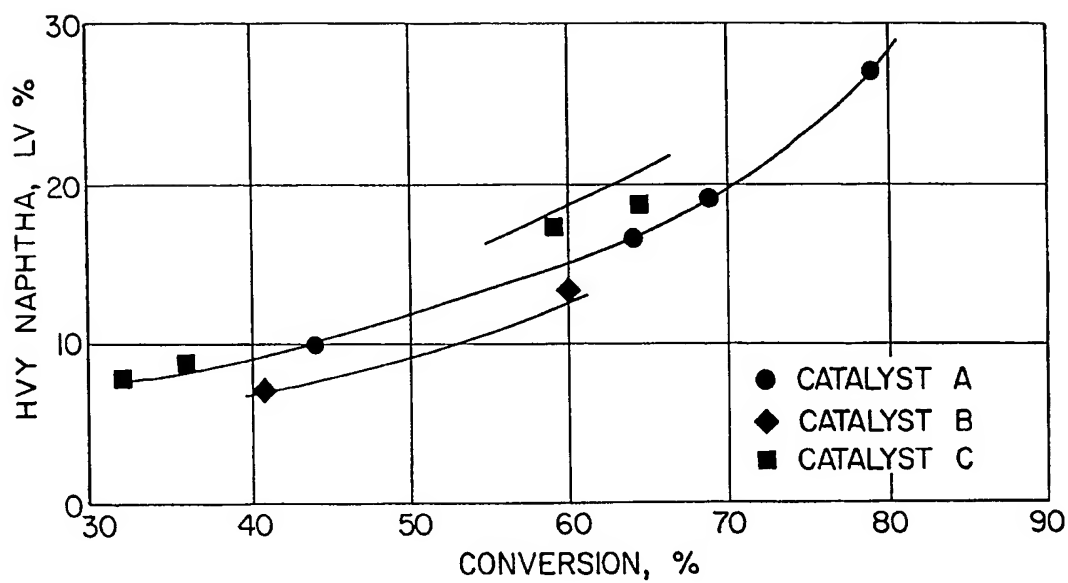


FIG.\_5.

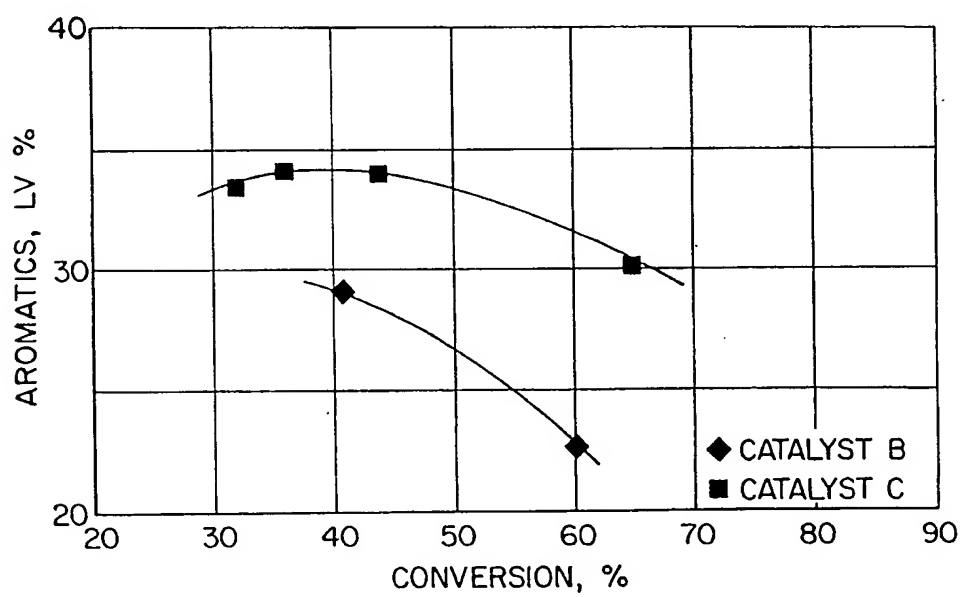


FIG.\_6.

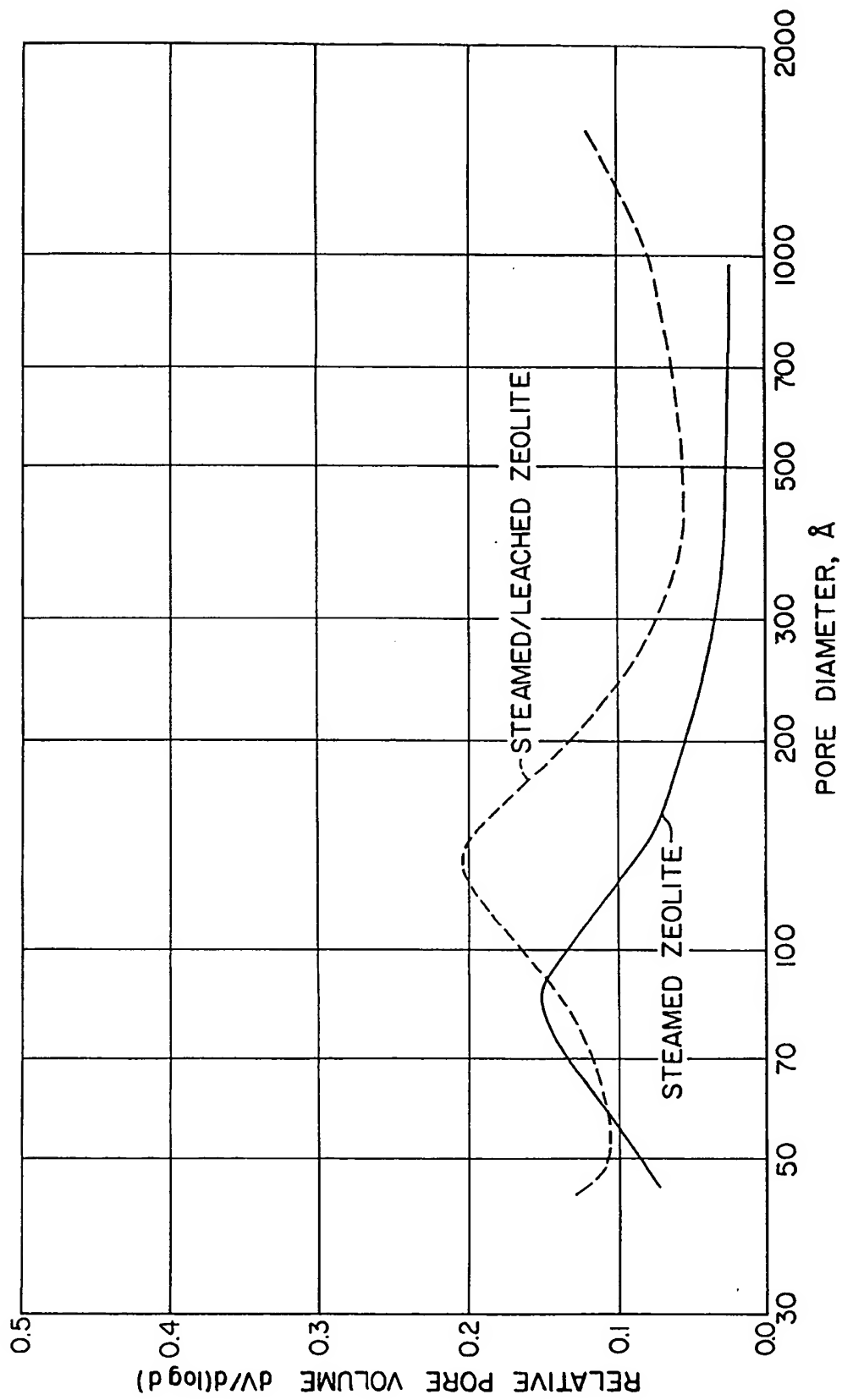


FIG.—7.

## SPECIFICATION

## Middistillate producti n

- 5 This invention relates to a process for selectively producing middistillate hydrocarbons. 5
- One of the most important characteristics that a modern petroleum refinery must have is flexibility. The ability to use different feedstocks, ranging from shale oils and heavy oils to light oils, to produce different product requirements in response to changing consumer demands is crucial to profitability. Feedstocks, for example, are now shifting to higher boiling, lower quality
- 10 mixtures having more metal, nitrogen and sulfur contaminants than feeds previously used. 10
- Forecasts of consumer demand are predicting shifts from gasoline-range hydrocarbons to heavier, higher boiling products such as diesel fuels, fuel oils and turbine fuels.
- Hydrocracking, used either in a one-step process or multistep processes coupled with hydrodesulfurization and hydrodenitrogenation steps, has been used extensively to upgrade
- 15 poor-quality feeds and to produce gasoline-range materials. Over the years, much development 15
- work has gone into finding improved hydrocracking conditions and catalysts. Tests have used catalysts containing only amorphous materials and catalysts containing zeolites composited with amorphous materials.
- Among the zeolites disclosed in the patent literature are Y (U.S. 3,130,007); decationized Y
- 20 (U.S. 3,130,006); ultrastable Y (U.S. 3,293,192 and U.S. 3,449,070); and ultrahydrophobic 20
- Y (U.K. 2,014,970 published September 5, 1979). Disclosures have appeared which relate to modifying zeolites. U.S. 3,367,884 discloses reducing the activity of superactive zeolites by a calcining, leaching procedure. The catalyst is disclosed as being especially useful for cracking gas oils to gasoline. U.S. 3,506,400 and U.S. 3,591,488 disclose improving the stability of
- 25 the crystalline lattice of zeolites by a steaming and acid extraction process. The product, a 25
- stabilized zeolite, may be used in hydrocracking and is disclosed as having improved selectively as shown by higher gasoline yield and lower coke make.
- Other research has resulted in disclosures relating to producing midbarrel products. U.S. 3,853,72 discloses hydrocracking high boiling feeds to produce midbarrel products using a
- 30 catalyst improving the production of midbarrel products by hydrocracking with a catalyst 30
- containing a steamed zeolite.
- We have discovered that middistillate products can be selectively produced by hydrocracking with an expanded-pore zeolitic catalyst.
- Thus in accordance with the present invention, there is provided a process for selectively
- 35 producing middistillate hydrocarbons, comprising: 35
- (a) contacting under hydrocracking conditions a hydrocarbonaceous feed boiling above 600°F (316°C) with a catalyst comprising a hydrogenation component and an expanded pore zeolite which consists of a faujasitic zeolite which has been steamed and then dealuminated; and
- (b) recovering a hydrocarbonaceous effluent of which more than 40 percent by volume boils
- 40 above 300°F (149°C) and below 700°F (371°C). 40
- We have discovered that faujasitic zeolites which have been dealuminated after high-temperature steaming have surprising stability and activity for producing middistillates from higher-boiling feeds. By faujasitic zeolites are meant crystalline aluminosilicates, synthetic or natural, which have the crystalline structure of the large-pore zeolite, faujasite. These zeolites
- 45 include faujasite, zeolite X, zeolite Y, and zeolites derived from them. For example, there are 45
- numerous processes known to the art for treating zeolite Y to produce "decationized Y", "ultrastable Y", "Z14-US", and others. The preferred faujasitic zeolite is zeolite Y, as well as derivative zeolites having the crystal lattice characteristics of zeolite Y. The most preferred faujasitic zeolite is an ultrastable Y zeolite having a sodium content of less than 0.5 wt. % (as Na<sub>2</sub>O).
- 50 As prepared, the large pore zeolites typically contain significant amounts of alkali metal. 50
- Because the alkali metals tend to poison the acid sites of the zeolite, standard ion-exchange procedures are used to remove them. The alkali metal content (calculated as oxide) is preferably reduced to below 5 weight percent before any heat treatments, and to less than 200ppm by weight in the final zeolite.
- The faujasitic zeolite being treated is calcined at high temperatures in the presence of water
- 55 which is preferably stagnant. During this high-temperature steaming, it is desired that at least 2 55
- weight percent of the atmosphere above the zeolite be water, preferably more than 10 weight percent, more preferably greater than 25 weight percent. The most convenient way to calcine the zeolite is to place the zeolite which has undergone aqueous ion exchange into an autoclave
- 60 and allow steaming to take place under autogenous pressure. The temperature of the steaming 60
- step is normally above 1000°F (538°C), preferably above 1200°F (649°C), and most preferably above 1400°F (760°C). The time of the steam calcining can range from one-half hour to twenty-four hours or more.
- It appears that the steam calcining causes aluminum to be removed from the crystal lattice
- 65 and silicon to be volatilized to repair the holes left in the lattice by the aluminum. Thus, the 65

integrity of the lattice is largely maintained and total collapse is avoided. Nevertheless, there is some loss of crystallinity. The steaming also creates gross cracks and fissures in the crystalline particles. The aluminum removed from the lattice appears to form amorphous alumina deposits in the lattice pores and channels. These amorphous deposits are removed by the dealumination procedure. Dealumination typically involves leaching the steamed zeolite with organic chelating agents such as EDTA or with organic or inorganic acids. Dilute inorganic acids, particularly hydrochloric acid and sulfuric acid, are most preferred. Where acids are used, the pH of the leaching solution is preferably below about 2. It can be appreciated that if the pH is too high, dealumination will take inconveniently long, while if the acid concentration is too high, the zeolite's crystal lattice can be attacked. Typical acid solutions are from about 0.01N to about 10N.

The final zeolitic product will have a smaller crystal lattice and a higher silica: alumina mole ratio than is normally obtained. Steamed, dealuminated zeolite Y will typically have a cubic cell constant less than about 24.40 Angstroms and a silica:alumina mole ratio greater than about 10:1, and most preferably greater than about 20:1. The final dealuminated product will also have a higher surface area than the starting material. The steaming/calcining treatment surprisingly also improves the catalytic characteristics of ultrastable Y zeolites. Even though the alumina content of the steamed-leached faujasitic zeolites is very low compared to the starting materials, they retain surprising activity and they gain significant selectivity for the valuable middistillates.

The final catalyst composite includes both the faujasitic zeolite and an inorganic oxide matrix. Inorganic oxides are standard supports for zeolites used in hydroprocessing and can include alumina, silica, magnesia, titania, and combinations thereof. The preferred support is alumina. A wide variety of procedures can be used to combine the zeolite with the refractory oxide. For example, the zeolite can be milled with a hydrogel of the oxide followed by partial drying if required and extruding or pelletizing to form particles of the desired shape. Alternatively, the refractory oxide can be precipitated in the presence of the zeolite. This is accomplished by increasing the pH of the solution of a refractory oxide precursor such as sodium aluminate or sodium silicate. As described above, the combination can then be partially dried as desired, tableted, pelleted, extruded, or formed by other means and then calcined, e.g., at a temperature above 600°F (316°C), usually above 800°F (427°C). Processes which produce larger pore size supports are preferred to those producing smaller pore size supports when cogelling. Additionally, if the steamed zeolite is added to an acidic solution of inorganic oxide precursor, the leaching step can be carried out in situ in the cogellation mixture without a separate leaching step.

The catalyst should contain less than about 50, preferably less than about 30 weight percent of the zeolite based on the dry weight of zeolite and refractory oxide. However, zeolite content should exceed 0.5 and is usually above 2 weight percent.

The final catalyst composite includes at least one hydrogenation component. The hydrogenation component is typically a transition or Group IV-A metal, and is usually a Group VI-B or VIII metal or combination of metals of their oxides or sulfides.

The hydrogenation components preferably are molybdenum, tungsten, nickel and cobalt metals, oxides and sulfides. Preferred compositions contain more than about 5 weight percent, preferably about 5 to about 40 weight percent molybdenum or tungsten or both, and at least about 0.5, and generally about 1 to about 15 weight percent of nickel or cobalt or both, determined as the corresponding oxides. The catalysts are often presulfided before use as sulfide form of these metals tends to have higher activity, selectivity and activity retention.

The hydrogenation components can be added by any one of numerous procedures. They can be added either to the zeolite or the support or a combination of both. In the alternative, the Group VIII components can be added to the zeolite by comulling, impregnation, or ion exchange and the Group VI components, i.e., molybdenum and tungsten, can be combined with the refractory oxide by impregnation, comulling or co-precipitation.

The hydrogenation components can be incorporated at any one of a number of stages in the catalyst preparation. For example, metal compounds such as the sulfides, oxides or water-soluble salts such as ammonium heptamolybdate, ammonium tungstate, nickel nitrate and cobalt sulfate can be added by comulling, impregnation or precipitation to either the zeolite or the refractory oxide or both before the zeolite is finally calcined and combined with the support or after its final calcination but before combination with the refractory oxide. These components can be added to the finished catalyst particle by impregnation with an aqueous or hydrocarbon solution of soluble compounds or precursors.

The hydrocarbonaceous feeds used in these processes boil primarily above about 600°F (316°C), generally above 700°F (371°C). Preferably, at least about 90 percent of the feed will boil between about 700°F (371°C) and about 1200°F (649°C). Feedstocks having these characteristics include gas oils, vacuum gas oils, coker gas oils, deasphalted residua and catalytic cracking cycle stocks. The feed to the hydrocracking zone generally contains at least

about 5 ppm and usually between about 10 ppm and 0.1 weight percent nitrogen as organonitrogen compounds. It can also contain substantial amounts of mono- or polynuclear aromatic compounds corresponding to at least about 5, and generally about 5 to about 40 volume percent aromatics.

5 Although the catalysts used in these methods exhibit superior stability, activity and midbarrel selectivity, reaction conditions must nevertheless be correlated to provide the desired conversion rates while minimizing conversion to less desired lower-boiling products. The conditions required to meet these objectives will depend on catalyst activity and selectivity and feedstock characteristics such as boiling range, as well as organonitrogen and aromatic content and  
10 structure. They will also depend on the most judicious compromise of overall activity, i.e., conversion per pass and selectivity. For example, these systems can be operated at relatively high conversion rates on the order of 70, 80 or even 90 percent conversion per pass. However, higher conversion rates generally result in lower selectivity. Thus, a compromise must be drawn between conversion and selectivity. The balancing of reaction conditions to achieve the desired  
15 objectives is part of the ordinary skill of the art.

Reaction temperatures generally exceed about 500°F (260°C) and are usually above about 600°F (316°C), preferably between 600°F (316°C) and 900°F (482°C). Hydrogen addition rates should be at least about 400, and are usually between about 2,000 and about 15,000 standard cubic feet per barrel. Reaction pressures exceed 200 psig (13.7 bar) and are usually  
20 within the range of about 500 to about 3000 psig (32.4 to 207 bar). Liquid hourly space velocities are less than about 15, preferably between about 0.2 and about 10.

The overall conversion rate is primarily controlled by reaction temperature and liquid hourly space velocity. However, selectivity is generally inversely proportional to reaction temperature. It is not as severely affected by reduced space velocities at otherwise constant conversion.

25 Conversely, selectivity is usually improved at higher pressures and hydrogen addition rates. Thus, the most desirable conditions for the conversion of a specific feed to a predetermined product can be best obtained by converting the feed at several different temperatures, pressure, space velocities and hydrogen addition rates, correlating the effect of each of these variables and selecting the best compromise of overall conversion and selectivity.

30 The conditions should be chosen so that the overall conversion rate will correspond to the production of at least about 40 percent, and preferably at least about 50 percent of products boiling below about 700°F (371°C) per pass. Midbarrel selectivity should be such that at least about 40, preferably at least about 50 percent of the product is in the middistillate range. The process can maintain conversion levels in excess of about 50 percent per pass at selectivities in  
35 excess of 60 percent to middistillate products boiling between 400°F (204°C) and 700°F (371°C).

The process can be operated as a single-stage hydroprocessing zone. It can also be the second stage of a two-stage hydrocracking scheme in which the first stage removes nitrogen and sulfur from the feedstock before contact with the middistillate-producing catalyst. The process  
40 can also be the first stage of a multistep hydrocracking scheme. In operation as the first stage, the middistillate-producing zone also denitrifies and desulfurizes the feedstock; in addition, it allows the second stage to operate more efficiently so that more middistillates are produced overall than in other process configurations. This method of operating with the middistillate-producing zone is especially preferred for increasing middistillate production.

45 In the accompanying drawings,

*Figure 1* illustrates the difference in fouling rate and activity between a standard amorphous catalyst used to produce middistillates and the catalyst used in the invention.

*Figure 2* illustrates the effect of the amount of acid used in the leaching solution on the silica:alumina mole ratio of the zeolite.

50 *Figure 3* illustrates the effect of the amount of acid used in the leaching solution on the crystallinity of the product zeolite as compared to the reactant steamed zeolite.

*Figures 4, 5, and 6* illustrate the superiority of the invention in producing middistillate.

Catalysts containing steamed/leached, steamed, and untreated ultrastable Y zeolites were contrasted. Fig. 4 illustrates the higher middistillate diesel yields of the steamed/leached catalyst; Fig. 5 illustrates the lower heavy naphtha yields of the steamed/leached catalyst; and  
55 Fig. 6 illustrates the lower aromatics content of the middistillate produced by the steamed/leached catalyst. The yields are plotted against conversion to below 670°F (354°C).

*Figure 7* contrasts the pore size distribution of a steamed and steamed/leached Y zeolite.

The following Examples illustrate the invention.

60 *Example 1*

A catalyst containing steamed, leached Y zeolite was compared to a nickel-tungsten, nonzeolitic catalyst (silica/alumina/titania cogel base) used to prepare middistillates to compare activity and fouling rates. The zeolitic catalyst contained 15 weight percent zeolite steamed at  
65 1475°F (802°C) for 1 hour and washed with 1 N hydrochloric acid. The zeolite was mulled with



alumina and had a final metals content of 3.9 weight percent nickel and 20.5 weight percent tungsten. The feed was a straight-run Arabian Heavy gas oil having the following characteristics:

	°API	21.8	
5	Aniline Pt.	173°F (78°C)	5
	S, Wt. %	2.62	
	N, ppm	846	
	Distillation (D-1160), °C:		
10	St/5	332/338	10
	10/30	401/436	
	50	451	
	70/90	468/499	
	95/EP	514/540	

Reaction conditions included an LHSV of 0.75; 1400 psig (96.5 bar); and 5000 SCF H<sub>2</sub>/bbl feed. The results are shown in Fig. 1. The zeolitic catalyst is significantly more active with a significantly lower fouling rate than the nonzeolitic catalyst.

#### 20 Example 2 20

A series of experiments was performed to examine the effect of acid washing on silica: alumina mole ratio and product zeolite crystallinity. The starting material was NH<sub>4</sub>Y having a sodium content of less than 1 percent and a silica: alumina mole ratio of 5.1:1. The zeolite was steamed for 1 hour at 800°C and then acid washed. The washing solutions were prepared on the basis of volumes of concentrated hydrochloric acid per gram of the zeolite (0.8 ml concentrated HCl is the stoichiometric amount of acid required to raise the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> mole ratio from 5:1 to 30:1), the measured acid was then diluted to about 1.1 M or 8.5 M and zeolite was washed with the resulting solution. The silica:alumina mole ratio was determined by neutron activation analysis; percent crystallinity was measured as percent X-ray diffraction intensity relative to Na-Y. As can be seen from FIGS. 2 and 3, SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> mole ratio and percent crystallinity appear to vary linearly and unexpectedly with the amount of acid used to prepare the washing solution rather than with the strength of the washing solution. It is preferred to retain at least 50 percent crystallinity measured as percent X-ray diffraction intensity relative to Na-Y in the products as compared to the starting material.

#### 35 Example 3 35

A series of experiments was performed to compare the products obtained with different zeolitic hydrocracking catalysts. Catalysts A and B were steamed for 1 hour at 800°C and Catalyst B was leached with 1 N hydrochloric acid to remove the alumina debris. The zeolites were composited with alumina by comulling and then extruded. The extrudate was impregnated with the hydrogenation metals using standard procedures. The catalysts had the following characteristics:

45	A	B	C	45
	Steamed	Steamed/	Ultra-	
Catalyst	Ultra-	Dealuminated	stable Y	
Zeolite	stable Y	Ultra-		
		stable Y		
Wt. % Zeolite	15	15	15	
50 Wt. % Ni	6.9	4.0	3.4	50
Wt. % W	17.2	21.0	20.0	
Cell Constant, Å	24.44	24.36	24.58	
SiO <sub>2</sub> :Al <sub>2</sub> O <sub>3</sub>	5:1	29:1	5:1	

55 The catalysts were tested in a one-step hydrocracking process using a straight-run Arabian Light vacuum gas oil feed having the following characteristics: 55

	*API	22.9	
	Aniline Pt., °F (°C)	177.5 (81°C)	
	S, weight percent	2.15	
5	N, ppm	877	5
	Distillation (D-1160), °C:		
	St/5	339/374	
	10/30	381/413	
10	50	448	10
	70/90	467/503	
	95/EP	511/536	

Reaction conditions included an LHSV of 1.2; 1470 psig H<sub>2</sub> (101 bar); and 5000 SCF/bbl feed recycle gas. 15

The highly desirable product characteristics produced by the process of the invention are illustrated in Figs. 4, 5, and 6. The steamed/leached zeolite produces significantly more middistillate (Fig. 4) of lower aromatics content (Fig. 6) than the steamed and untreated Y zeolite. Additionally, cracking of the feed to naphtha-range materials occurs to a significantly lower extent (Fig. 5) with the steamed/dealuminated zeolite catalyst. 20

#### Example 4

A steamed (1375°F; 746°C) Y zeolite having a silica:alumina mole ratio of 5.1:1 was washed with an approximately 1 M HCl solution (0.74 cc concentrated HCl/g zeolite). The leached product had a silica: alumina mole ratio of 9.6:1. The pore size distributions for both materials (relative pore volume dV/d (log d) as a function of pore diameter) are contrasted in Fig. 7. 25

#### CLAIMS

1. A process for selectively producing middistillate hydrocarbons, comprising:
  - 30 (a) contacting under hydrocracking conditions a hydrocarbonaceous feed boiling above 600°F (316°C) with a catalyst comprising a hydrogenation component and an expanded pore zeolite which consists of a faujasitic zeolite which has been steamed and then dealuminated; and
    - (b) recovering a hydrocarbonaceous effluent of which more than 40 percent by volume boils above 300°F (149°C) and below 700°F (371°C).
  - 35 2. A process according to Claim 1, wherein said faujasitic zeolite is a Y zeolite.
  3. A process according to Claim 2, wherein said faujasitic zeolite is an ultrastable Y zeolite.
  4. A process according to Claim 3, wherein said faujasitic zeolite has a sodium oxide content of less than 0.5 wt. %.
  5. A process according to Claim 2, 3, or 4, wherein said expanded pore zeolite has a cubic cell constant less than 24.40 Angstroms and a silica to alumina mole ratio greater than 10:1. 40
  6. A process according to Claim 5, wherein said silica to alumina mole ratio is greater than 20:1.
  7. A process according to any preceding claim, wherein said expanded pore zeolite contains less than 200 ppm by weight of alkali metal oxide.
  - 45 8. A process according to any preceding claim, wherein said faujasitic zeolite is dealuminated by contacting the steamed faujasitic zeolite with an acid at a pH less than 2.
  9. A process according to any preceding claim, wherein said faujasitic zeolite is steamed at a temperature above 1000°F (538°C).
  10. A process according to any preceding claim, wherein said steaming is effected in a stagnant manner. 50
  11. A process according to any preceding claim, wherein said hydrogenation component is nickel, cobalt, molybdenum, or tungsten or an oxide or sulfide thereof, or mixtures thereof, and said catalyst further comprises an inorganic oxide matrix.
  12. A process according to Claim 11, wherein said matrix is alumina.
  - 55 13. A process according to any preceding claim, wherein said feed boils above 700°F (371°C) and more than 60 percent by volume of said effluent boils between 400°F (204°C) and 700°F (371°C).
  14. A process according to Claim 13, wherein said feed is a gas oil.
  15. A process according to any preceding claim and further comprising the step of (c) hydrocracking at least part of said hydrocarbonaceous effluent. 60
  16. A process in accordance with Claim for selectively producing middistillate hydrocarbons substantially as described in any one of the foregoing Examples.